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54) Title: Laundry additive composition

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22) Application: Showa 59(1984), July 20

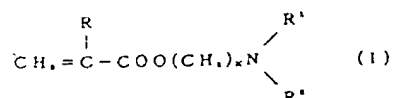
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7-3, Honjo-1, Sumida-ku, TokyoDETAILED DESCRIPTION1. Title of the invention

Laundry additive composition

2. Patent Claim

1. Laundry additive composition in which a CO<sub>2</sub>-containing compound and an acidic compound are coated or contained in copolymer which is made of

(A) One kind of a basic monomer according to general formula (I)



(in the formula R stands for a hydrogen or a methyl group, R<sup>1</sup> and R<sup>2</sup> are alkyl groups with 1-3 carbon atoms and x is an integer from 1 to 4).

(B) At least 1 water-insoluble or sparingly soluble monomer, and

(C) at least 1 water-soluble monomer.

### 3. Detailed explanation of the invention

#### Application in industry

This invention is concerned with laundry additive compositions, particularly laundry additive compositions to be used with alkaline detergents.

#### Conventional technique

Generally, in the washing process, a washing machine is filled with water, followed by washing, removal of the water, rinsing, again removal of the water, adding laundry additives such as softeners during the washing cycle. Previously, the housewife usually had to operate the machine through each process and thus it was not a problem to add the detergent during the washing process and then add the softener, bleach, starch etc., during the rinsing process. Recently, however, semiautomatic or automatic washing machines have been developed and the housewife has been released from such stepwise operation in the addition of laundry additives.

Thus, the laundry additives that are introduced with the detergent must be protected during the washing cycle, carried over into the rinsing step and it is necessary for these to dissolve in the water during the rinsing step.

#### Problems to be solved by this invention

If the laundry additive is covered by a polymer which is insoluble in the alkaline washing solution, but soluble in the neutral rinsing solution, the laundry additive will be protected from the alkaline washing solution and then it will dissolve in the rinsing solution during the rinsing step. By this method, the effect of the laundry additives can develop and manual addition is omitted conveniently, since the additive is introduced at the beginning with the detergent.

Polymers with pH-dependent solubility have been known. For example, polyvinyl acetal diethylaminoacetate is insoluble in neutral aqueous solution, but dissolves under acidic conditions when the pH drops below 5.8. Copolymers of vinylpyridine and acrylic acid are soluble below pH 4 and above pH 7.4, but they are insoluble between these two pH values. However, polymers which are soluble in the neutral or acidic range, but insoluble in the alkaline range and

which change their solubility in a narrow pH range have not been known. The Applicant proposed previously a laundry additive coated with such a copolymer in Patent Showa 58-247997, and this invention is an improvement of that invention, by providing an improved laundry additive coated with this polymer.

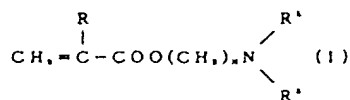
In the home, tap water is used for rinsing. The temperature of this tap water changes in the winter and summer. Generally, the temperature for rinsing ranges between 5-30°C. In order for the laundry additive to be effective, this laundry additive must dissolve at a certain rate regardless of the temperature.

Method to solve the problem

This invention offers a laundry additive which is protected in alkaline solution, but dissolves in the rinsing solution and exhibits their effect. The solubility of this laundry additive is constant regardless of the temperature of the rinsing solution.

The laundry additive composition of this invention is coated with a copolymer made of monomers (A) to (C). This laundry additive contains a CO<sub>2</sub>-containing compound and an acidic compound and is coated with the copolymer or is contained in the abovementioned copolymer.

(A) At least one basic monomer corresponding to the general formula I



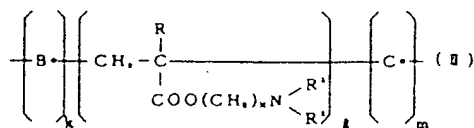
(in this formula, R is a hydrogen or methyl group, R<sup>1</sup> and R<sup>2</sup> alkyl groups with 1-3 carbon atoms, x is an integer from 1-4).

(B) At least one monomer which is insoluble or sparingly soluble in water, and

(C) at least one water-soluble monomer.

The abovementioned copolymer is practically insoluble in an alkaline aqueous solution but is soluble in a neutral or acidic aqueous solution. The laundry additive composition is insoluble in an alkaline solution above pH 9.5 but is soluble in mildly alkaline or acidic solution below pH 8.5 and preferably has a larger solubility ratio in the presence of a surfactant. From this point of view, the ratio of (a) in the copolymer is appropriately in the range of

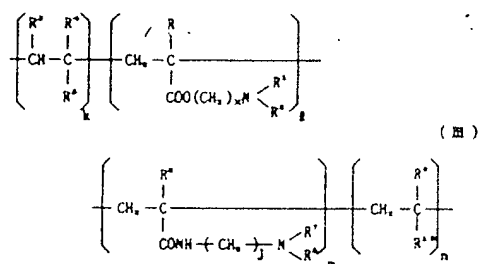
$k/(k + l + m) = 0.05-0.8$ ,  $l/(k + l + m) = 0.05-0.8$  in the general formula (II), and preferably  $k/(k + l + m) = 0.05-0.6$ ,  $l/(k + l + m) = 0.1-0.7$ .



(In the formula, B\* and C\* are units of monomer (B) and (C), respectively).

Also, it is suitable for the degree of polymerization to be such that  $k + l + m = 100-50,000$ , preferably  $300-20,000$ .

A suitable example of this copolymer is shown by general formula (III)



where  $\text{R} = \text{H}$  or  $-\text{CH}_3$

$\text{R}^1 = \text{C}_1-\text{C}_3$  alkyl group

$\text{R}^2 = \text{C}_1-\text{C}_3$  alkyl group

$x = \text{integer from } 1-4$

$\text{R}^3 = \text{H}$  or  $\text{C}_1-\text{C}_4$  alkyl group

$\text{R}^4 = \text{H}$  or  $\text{C}_1-\text{C}_4$  alkyl group or  $-\text{COOR}^{11}$  ( $\text{R}^{11}$  is a  $\text{C}_1-\text{C}_{18}$  group)

$\text{R}^5 = -\text{COOR}^{12}$ ,  $-\text{OCOR}^{12}$  ( $\text{R}^{12}$  is a  $\text{C}_1-\text{C}_{18}$  alkyl group),  $-\text{C}_6\text{H}_5$

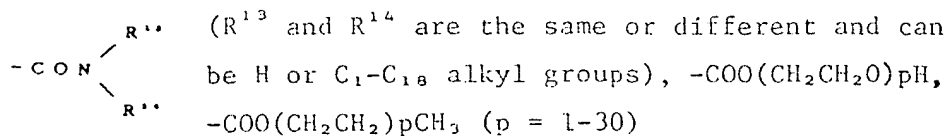
$\text{R}^6 = \text{H}$  or  $\text{C}_1-\text{C}_4$  alkyl group

$\text{R}^7, \text{R}^8 = \text{the same or different } \text{C}_1-\text{C}_4$  alkyl group

$J = \text{integer from } 1-4$

$\text{R}^9 = \text{H}$  or  $\text{C}_1-\text{C}_4$  alkyl group

$\text{R}^{10} = -\text{OH}$ ,  $-\text{CN}$ ,  $-(\text{CH}_2)_y\text{OH}$  ( $y = 1-4$ ),



$$k/(k + l + m + n) = 0.05-0.8$$

$$l/(k + l + m + n) = 0.05-0.8$$

$$m/(k + l + m + n) = 0.05-0.8$$

$$n/(k + l + m + n) = 0-0.5$$

Among these, the more preferable copolymers with a 4th component ( $n \neq 0$ ) and without a 4th component are as follows:

(1) With a 4th component,

$$R = H, -CH_3$$

$$R^1 = -CH_3 \text{ or } -C_2H_5$$

$$R^2 = -CH_3 \text{ or } -C_2H_5$$

$$R^3 = H$$

$$R^4 = H, -CH_3, -COOR^{11} \text{ (} R^{11} \text{ is a } C_1-C_8 \text{ alkyl group)}$$

$$R^5 = -COOR^{12} \text{ (} R^{12} \text{ is a } C_1-C_8 \text{ alkyl group) or } OCOCH_3$$

$$R^6 = H, -CH_3$$

$$R^7, R^8 = -CH_3, -C_2H_5$$

$$J = 1-4$$

$$R^9 = H, -CH_3$$

$$R^{10} = -COO(CH_2CH_2O)_pH \text{ (where } p = 1-5), -COO(CH_2CH_2O)_pCH_2 \text{ (where } p = 1-5), -CON(CH_3)_2, -CON(C_2H_5)_2$$

$$k/(k + l + m + n) = 0.05-0.5$$

$$l/(k + l + m + n) = 0.1-0.65$$

$$m/(k + l + m + n) = 0.1-0.6$$

$$n/(k + l + m + n) = 0.01-0.5$$

(2) Without a 4th component ( $n = 0$ )

$$R = H, -CH_3$$

$$R^1 = -CH_3, -C_2H_5$$

$$R^2 = -CH_3, -C_2H_5$$

$$R^3 = H$$

$$R^4 = H, -CH_2, -COOR^{11} \text{ (} R^{11} \text{ is a } C_1-C_8 \text{ alkyl group)}$$

$$R^5 = -COOR^{12} \text{ (} R^{12} \text{ is a } C_1-C_8 \text{ alkyl group) or } -OCOCH_3$$

$$R^6 = H, -CH_3$$

$$R^7, R^8 = -CH_3, -C_2H_5$$

$$J = 1-4$$

$$k/(k + l + m) = 0.05-0.6$$

$$l/(k + l + m) = 0.1-0.7$$

$$m/(k + l + m) = 0.1-0.7$$

Actual examples of monomers (A), (B) and (C) are as follows:

The basic monomer (the 2nd component in general formula (III) shown as (A) in general formula (I) is the main monomer for obtaining the pH-sensitive copolymer of this invention. Examples of such compounds are N,N-dimethylaminoethyl acrylate, N,N-dimethylaminomethyl acrylate, N,N-dimethylaminobutyl acrylate, N,N-dimethylaminopropyl acrylate, N,N-dimethylaminoethyl methacrylate, N,N-dimethylaminomethyl methacrylate, N,N-dimethylaminopropyl methacrylate, N,N-diethylaminoethyl acrylate, N,N-diethylaminomethyl acrylate, N,N-diethylaminobutyl acrylate, N,N-diethylaminopropyl acrylate, N,N-diethylaminoethyl methacrylate, N,N-diethylaminobutyl methacrylate, N,N-dimethylaminopropyl methacrylate, etc. These compounds can be used singly or as a mixture of 2 or more.

The water-insoluble or sparingly soluble monomer (B) (the 1st component in general formula (III)) contributes to enlarging the insoluble pH range of the sensitive copolymer. Examples of these are acrylate esters, methacrylate esters, crotonate esters, itaconate esters, vinyl acetate and styrenes and these can be used singly or as a mixture of 2 or more. When the alkyl ester of acrylic acid, methacrylic acid, crotonic acid or itaconic acid is used as monomer (B), the alkyl group of the ester may have 1-18 carbon atoms. However, when the alkyl chain becomes longer, the solubility of the copolymer in mildly alkaline solution becomes slower. Thus, it is preferable to have an alkyl group with a carbon chain of 1-8 carbon atoms. Preferable examples are methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate and ethyl methacrylate.

The water-soluble monomer (C) (the 3rd and 4th components of general formula (III)) contributes to the expansion of the soluble pH region of the pH-sensitive copolymer. Actual examples of these are: N,N-dimethylaminopropylacrylic acid (or methacrylic acid) amide, N,N-dimethylaminomethylacrylic acid (or methacrylic acid) amide, N,N-dimethylaminoethylacrylic acid (or methacrylic acid) amide, N,N-dimethylaminobutylacrylic acid (or methacrylic acid) amide, N,N-dimethylaminoacrylic acid (or methacrylic acid) amide, 2-hydroxyethylacrylic acid (or methacrylic acid), 2-hydroxypropylacrylic acid (or methacrylic acid),

polyethylene glycol or methoxypolyethylene glycol (in all these, ethylene glycol may be added, the average number of adduct being 1-30) per acrylic acid or methacrylic acid ester. These can be used singly or in mixtures of 2 or more.

The copolymers used in this invention are obtained by the usual radical polymerization methods under normal or high pressure, using acetone or others as solvent for the polymerization and azobisisobutyronitrile as polymerization initiator.

The polymerization temperature and time depend on the solvent used for the polymerization and on the combination of monomers. Generally it is 40-90°C and 5-20 hours.

The laundry additives covered by this invention are softeners, such as di-long-chain alkyl dimethylammonium salts, 1-methyl-1-long-chain alkanoylamino-ethyl-2-long-chain alkylimidazolinium salts di-long-chain-alkyl dimethylammonium salts and fatty acid salt mixtures. Antifoaming agents, silicone oil, bleaches, such as sulfite, percarbonate, organic peracids, starch, bluing agents, fluorescent brighteners, enzymes, etc., can be added.

Furthermore, the laundry additive composition of this invention contains a CO<sub>2</sub>-containing compound and an acidic compound. These compounds are covered by the copolymer together with the laundry additive or are contained in the copolymer covering the laundry additive. Also, either the CO<sub>2</sub>-containing compound or the acidic compound can be mixed with the copolymer and the laundry additives and the remaining ones are coated by the above mixture.

CO<sub>2</sub>-containing compounds are those containing CO<sub>2</sub> in the molecule, preferably carbonates or bicarbonates. Their salts are suitably alkali metal, alkaline-earth metal salts, preferably sodium, potassium or magnesium salts. As the acidic compound, an inorganic compound which is solid at room temperature is suitable and it should preferably be sparingly soluble or insoluble in organic solvents such as acetone, alcohol, etc., for the purpose of the production of the laundry additive composition.

Practical examples of such acidic inorganic compounds are: boric acid, metaphosphoric acid, pyrophosphoric acid, acid pyrophosphate, aluminum sulfate, bisulfites, dihydrogen phosphates, etc. Preferably, the acid pyrophosphate, bisulfite and dihydrogen phosphate are alkali metal or alkaline-earth metal salts.

The CO<sub>2</sub>-containing compound and the acidic compound are preferably present in the form of granules with a size less than 200  $\mu$ m or in the powdered form.

It is preferable to mix 100 parts by weight of copolymer with a total of 10-100 parts by weight of the CO<sub>2</sub>-containing compound and acidic compound, preferably 10-50 parts by weight. Less than 10 parts by weight is not sufficient to achieve the effect, but when 100 parts by weight are exceeded, this will destroy the film by it becoming practically soluble in the aqueous alkaline solution and the protective function of the film is reduced.

The mixing ratio of the CO<sub>2</sub> compound and the acidic compound is preferably such so that the dispersion has a pH of 5-8 when a total of 0.5 weight % are added. For example, when sodium bicarbonate or boric acid are used, the mixing ratio (sodium bicarbonate/boric acid) = 0.05-0.7 by weight in the case of aluminum sulfate the 14-18 H<sub>2</sub>O salt is used; (sodium bicarbonate)/(aluminum sulfate) = 0.4-0.9. When the mixing ratio is such that pH 8 is exceeded, the solubility of the laundry additive composition in the rinsing solution is reduced; however, if the pH is lower than 5, the above copolymer, which is practically insoluble in the alkaline solution, becomes soluble. These changes with regard to the solubility of the copolymer occur when only the acidic inorganic compound is used without the CO<sub>2</sub>-containing compound or if acetone, alcohol or organic acid solvents are used.

In order to produce the laundry additive composition of this invention, for example, 1-20 weight % of the copolymer of this invention is dissolved in an organic solvent, such as acetone, methanol, ethanol, isopropyl alcohol, benzene, chloroform, etc., and this solution is coated over a previously prepared granulated mixture of laundry additive, CO<sub>2</sub>-containing compound and acidic compound, using a pan or a fluidized bed.

In another method, the copolymer in a 30-60 weight % solution in an organic solvent, the CO<sub>2</sub>-containing compound, the acidic compound and the laundry additive are mixed. Then a part of the organic solvent is removed, the mixture is pulverized to form granules, the organic solvent is removed further to produce the copolymer-coated laundry additive composition.

In another method, the copolymer, in a 1-10 weight % organic solvent solution, the CO<sub>2</sub>-containing compound and the acidic compound are dispersed to obtain



the coating agent solution. Then the laundry additive granules are coated with this solution using a pan or fluidized bed.

The obtained coated laundry additive is preferably adjusted to have a grain size of 50-500  $\mu\text{m}$ . Also, the amount of coating is preferably 5-50 weight % of the laundry additive granules.

#### Action

According to this invention, the laundry additive is coated with a pH-sensitive copolymer. Thus, the laundry additive is protected in the alkaline washing solution and becomes active in the rinsing solution. At this time, the presence of the  $\text{CO}_2$  compound and acidic compound makes the solution rate constant regardless of the temperature of the rinsing solution.

The laundry additive composition of this invention is effective particularly when added to a granular anionic surfactant detergent. It is convenient to mix it with the detergent preliminarily. Naturally, it can be stored separately and added to the washing solution. It can also be used by itself without a detergent.

#### Effect

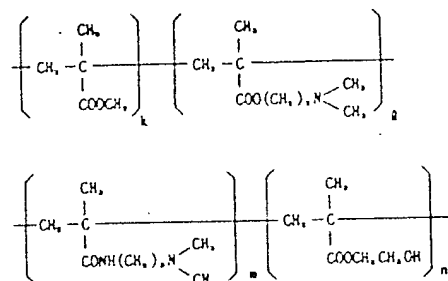
The laundry additive composition according to this invention is protected in the washing solution and the solution rate is constant in the rinsing solution regardless of temperature. Thus, seasonal temperature changes of the rinsing solution do not affect the rate of solution and the defined amount of additive effectively will exhibit the results.

### PRACTICAL EXAMPLES

#### Practical Example 1

The following were mixed to obtain a 40 weight % acetone solution: 45 parts by weight of the copolymer having the structure shown below, 40 parts by weight of distearyldimethylammonium chloride powder (grain size 20-100  $\mu\text{m}$ ), 4.8 parts by weight of silica powder, 7 parts by weight of sodium bicarbonate (grain size 20-100  $\mu\text{m}$ ), 3 parts by weight of aluminum sulfate $\cdot$ 14-18 $\text{H}_2\text{O}$  (grain size 20-100  $\mu\text{m}$ ), oil-soluble pigment No. 403, 0.2 parts by weight. Then the acetone content was reduced to 15-20 weight % in vacuo. The mixture was pulverized and the acetone was removed in a vacuum container while rotating the granules. The obtained laundry additive composition was covered with the

copolymer (blue-colored). The product was sieved through a 350-500  $\mu$ m size sieve. This laundry additive can be used as softener.



$[k/(k + l + m + n) = 0.35, l/(k + l + m + n) = 0.25, m/(k + l + m + n) = 0.3, k + l + m = 2000-3000]$ .

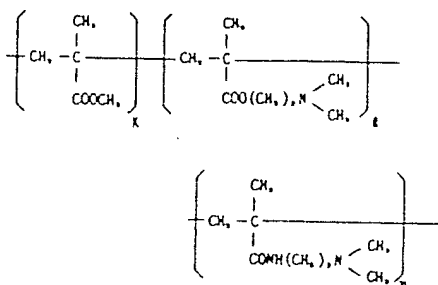
Commercial detergent (straight-chain sodium alkylbenzenesulfonate-containing heavy detergent), 40 g (water 30 L) was added to a washing machine containing clothes (cotton undershirts, 1 kg, nylon underwear, 0.2 kg). These were washed for 10 minutes and then spun. After spinning, the above laundry additive 1 g, was mixed with 30 L of water and the time needed to dissolve the laundry additive at a water temperature of 5-30°C was measured. The results are shown in Figure 1 together with Comparison Example 1.

#### Comparison Example 1

Using the above composition, 7 parts by weight of sodium bicarbonate and 3 parts by weight of aluminum sulfate $\cdot$ 14-18H<sub>2</sub>O were deleted from Practical Example 1. Otherwise, the method was carried out in the same manner as in Practical Example 1. The results are shown in Figure 1.

#### Practical Example 2

Distearyldimethylammonium chloride (100 parts by weight) was melted at 100-120°C and then it was mixed with sodium bisulfite powder (20 parts by weight) and sodium bicarbonate powder (16 parts by weight), followed by cooling to room temperature. The mixture was pulverized, sieved through a sieve to obtain 200-1000  $\mu$  granules. Then 30 parts by weight of this granulated mixture was coated with 70 parts by weight of the copolymer having the structure given below in a 10% acetone solution (also containing 0.2 parts by weight of blue pigment No. 403), using a pan-coating apparatus, to prepare the laundry additive composition.



$$[k/(k + l + n) = 0.4, l/(k + l + n) = 0.3, k + l + n = 1000-4000].$$

The dissolution time of this laundry additive composition was determined as shown in Practical Example 1 and the results are given in Table 1, together with Practical Example 3 and Comparison Examples 2 and 3.

#### Comparison Example 2

The procedure according to Practical Example 2 was followed except for the fact that the sodium bisulfite and sodium bicarbonate were omitted.

#### Practical Example 3

Distearyldimethylammonium chloride, 30 parts by weight (grain size 200-1000  $\mu\text{m}$ ) was placed in a pan-coating apparatus. The procedure was carried out as described in Practical Example 2, but 67.5 parts by weight of the copolymer in a 10% acetone solution (also containing 0.2 parts by weight of blue No. 403), 2 parts by weight of sodium bicarbonate and 0.5 parts by weight of anhydrous aluminum sulfate were mixed to coat distearyldimethylammonium chloride granules, to prepare a laundry additive composition. The dissolution time of this laundry additive in the rinsing solution was determined as shown in Practical Example 1.

#### Comparison Example 3

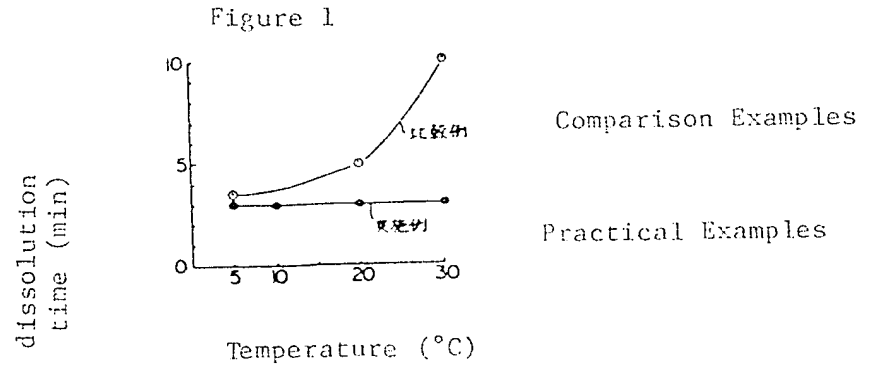
The procedure of Practical Example 3 was followed but the only difference was that the sodium bicarbonate and aluminum sulfate used in Practical Example 3 were omitted.

Table 1

	dissolution time (min)		
	5°C	10°C	30°C
Pract. Example 2	3.5	3.5	4
Comparison Ex. 2	5	7	12
Pract. Example 3	2.5	2.5	3
Comparison Ex. 3	3	5	10

#### 4. Brief explanation of the Figure

Figure 1 shows the relationship between the temperature of the rinsing solution and the rate of dissolution.



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